Kinetics of Esterification of Palmitic Acid with Isobutyl Alcohol on Ion-Exchange Resin Pellets

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Abstract

Cylindrical pellets were made by mixing ion-exchange resin particles with binding powders and heating to 140°C. To compare catalytic activities of these resin pellets with those of resin particles and sulfuric acid, the esterification of palmitic acid with isobutyl alcohol was carried out in a batch reactor. The rate equation for sulfuric acid could be applied to ion-exchange resins although the values of parameters were different.

Introduction

The use of a solid ion-exchange resin as catalyst has some advantages over a homogeneous catalyst, such as the catalyst can be easily separated from solutions and continuous operations in fixed-bed reactors are possible. However, since the diameter of conventional ion-exchange resin particles are less than 1 mm, the pressure drop may be very high in fixed-bed reactors packed with resin particles. To reduce the pressure drop, cylindrical pellets were made by mixing ion-exchange resin particles with binding powders and heating to 140°C. In our previous articles, the hydrolysis of ethyl formate was investigated in a batch reactor [1] and in a continuous flow reactor [2] to compare catalytic activities of resin pellets with those of resin particles.

The reaction between alcohol and carboxyl acid with acid catalyst to form ester and water is important from industrial point view. In our previous article [3], kinetics of the esterification of palmitic acid with isobutyl alcohol was studied by using sulfuric acid as homogeneous catalyst and reviewed critically.

To our knowledge, there are no publications on this esterification by using ion-exchange resins. In this article, the catalytic activity of ion-exchange resin pellets is compared with that of resin particles as well as the results of sulfuric acid in the previous article [3].

Other esterifications have been studied by using ion-exchange resins, for example, Roy and Bhatia [4] investigated the kinetics of esterification of benzyl alcohol with acetic acid on ion-exchange resin (Amberlyst 15) and sulfuric acid. Their rate data were correlated with kinetic model based on homogeneous reaction and sulfuric acid gave higher conversion than Amberlyst 15.

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Experimental

Strong cation exchange resin particles, Amberlyst 15 in the H^+ form, were used as a catalyst. The average diameter of particles was 0.61 mm. The ion-exchange capacity, Q_{particle}, was 4.96 mol/(kg-dry particle).

Cylindrical pellets with 5 mm diameter were made by mixing ion-exchange resin particles with 15 wt% polyethylene powders in the mold and heating to 140°C for one hour to bind particles with the diameter of 0.61 mm. Figure 1 shows the illustration of a pellet made of spherical resin particles. The ion-exchange capacity, Q_{pellet}, was 3.98 mol/(kg-dry pellet), which was smaller than that of particle. This decrease of capacity may be explained by adding binders to pellets.

Palmitic acid and ion-exchange resin particles were placed in a flask equipped with a stirrer, a condenser, and a thermometer. The stirring speed was kept at 300 rpm to suspend particles.

Since it was difficult to suspend pellets, a rotating basket reactor was used [5]. Two baskets packed with pellets were attached to the rotating axis and were rotated as a stirrer.

The reactor which contained palmitic acid and catalyst was heated in an oil bath up to the reaction temperature. The reaction was started by adding preheated isobutyl alcohol. The total volume of mixture, V, was 4.0×10^{-4} m^3.

A 2ml of the reaction mixture was sampled at various reaction time and titrated by 0.1N NaOH aqueous solution using phenolphthalein as an indicator. The relation between the conversion of palmitic acid, X_A, and the reaction time, t, was obtained.

In preliminary experiments, rotating speeds were varied from 200 to 500 rpm and catalyst diameters from 0.4 to 1.0 mm. Rate data were independent of rotating speeds and diameters within experimental ranges. Therefore, the resistances of liquid-solid mass transfer and intraparticle diffusion were negligible.

Results and Discussion

Catalytic Activity of Ion-Exchange Resin Particles

Figure 2 shows the effect of catalyst amount, W, for ion-exchange resin particles. The reaction rate is increased with the increase of catalyst particles. The effect of ratio of initial concentrations of isobutyl alcohol to

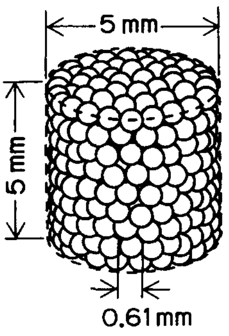

Figure 1. Pellet made of spherical resin particles.

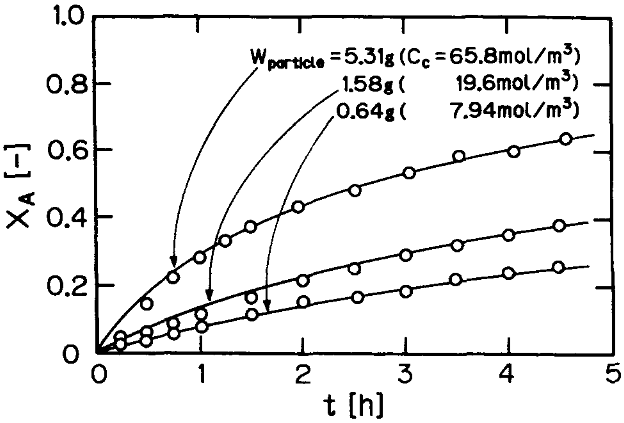

Figure 2. Effect of catalyst amount for resin particles. (T = 380 K, C_{AO} = 1250 mol/m^3, M = 5, and W_O = 0).

palmitic acid ($M = C_{BO}/C_{AO}$) is shown in Figure 3. The initial reaction rate is independent of M. However, the reaction time proceeds, the rate rapidly slows down for lower values of M.

These behaviors are almost the same as those of sulfuric acid in our previous article [3]. Then, the rate equation for Amberlyst 15 particles is assumed to be identical to eq. (22) in the previous article [3].

$$\text{Rate} = k(C_A C_B - C_E C_W/K)/(C_B + K_W C_W)$$

where $k = k_c C_c + k_b$.

The concentration of homogeneous catalyst, C_c, should be replaced to QW/V for the heterogeneous catalyst to keep the same concentration of catalyst. The rate constant, k_c, and the equilibrium constant of water adsorption, K_W, were adjusted to be fitted to experimental data while the equilibrium constant of reversible reaction, K, was fixed at the same value as sulfuric acid [3]. The fraction of water content at the initial condition, $W_O(= C_{WO}/C_{AO})$, was always zero because resins were used as dry states.

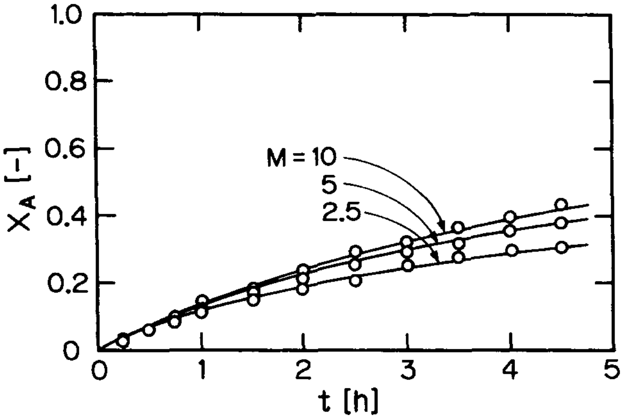

Figure 3. Effect of initial ratio of isobutyl alcohol to palmitic acid, M for resin particles. (T = 380 K, W_{particle} = 1.58 g, and W_O = 0).

When $k_c = 2.0 \times 10^{-6}$ m^3/(mol · s) and $K_W = 15$ at 380 K, the results calculated from the integrated form of rate equation, eq. (31) in the previous article [3], are in good agreement with experimental results, as shown in solid lines of Figures 2 and 3.

Catalytic Activity of Ion-Exchange Resin Pellets

Figures 4 and 5 show the effects of catalyst amount and the ratio, M, in the case of pellets. The behavior is also similar to those of sulfuric acid and may be explained by the same reaction mechanism as sulfuric acid although the values of parameters are different. The solid lines indicate the calculated results by using

$$k_c = 2.0 \times 10^{-6}\ \text{m}^3/(\text{mol} \cdot \text{s}) \quad \text{and} \quad K_W = 1 \text{ at } 380 \text{ K}.$$

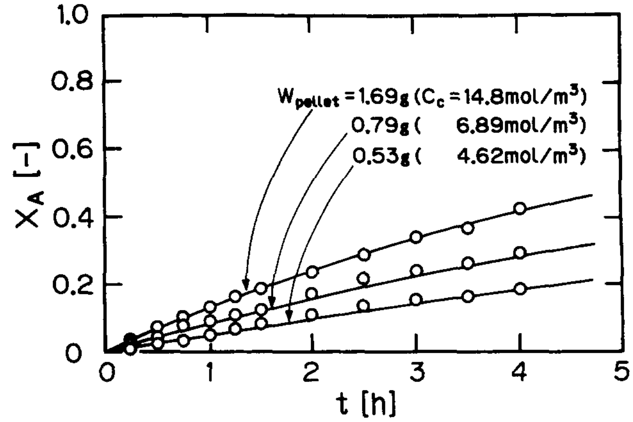

Figure 4. Effect of catalyst amount for resin pellets. (T = 380 K, C_{AO} = 1250 mol/m^3, M = 5, and W_O = 0).

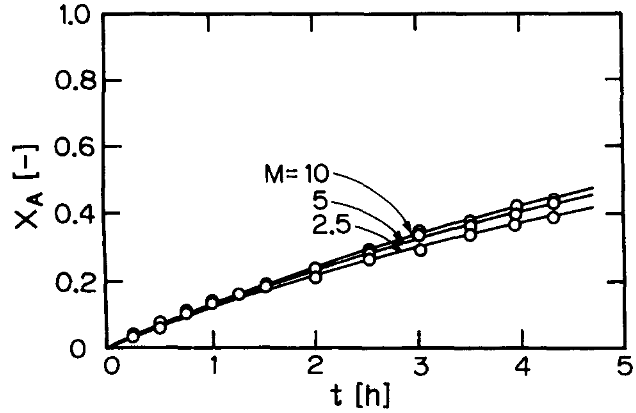

Figure 5. Effect of initial ratio of isobutyl alcohol to palmitic acid, M for resin pellets. (T = 380 K, W_{pellet} = 1.69 g, and W_O = 0).

TABLE I. Parameters at 380 K.

Catalyst	Q [mol/(kg-dry solid)]	k_c [m^3/(mol · s)]	K_w [−]
Sulfuric acid	–	1.5×10^{-4}	10
Particle	4.96	2.0×10^{-6}	15
Pellet	3.98	2.0×10^{-6}	1

Comparisons between Ion-Exchange Resins and Sulfuric Acid

Table I summarizes the parameters obtained from experimental results. The rate constant, k_c, for both particles and pellets is much smaller than that for sulfuric acid. This decrease may be explained by steric hindrance of ion-exchange resins because the palmitic acid, $CH_3(CH_2)_{14}COOH$, is a relatively large molecule. Also, Amberlyst 15 acts through the intermediary sulfonic groups bonded to insoluble macromolecule and the acid strength of ion-exchange resins is weaker than that of sulfuric acid. This behavior is similar to a previous work of Roy and Bhatia [4].

The equilibrium constant of water adsorption, K_W, for ion-exchange resin particles is larger than that of sulfuric acid due to the swelling of water into ion-exchange resin particles. On the other hand, K_W, for pellets, is much smaller than that for particles. This may be due to the hydrophobic property of polyethylene which is mixed as the binder. Therefore, water produced by the esterification can easily be removed from the interior of pellets. Figure 6 shows the comparisons of calculated results among three catalysts. The weights of particles and pellets are 5.31 g and the concentration of sulfuric acid, C_c, is calculated from $Q_{\text{particle}}W/V$. Since the catalytic activity of sulfuric acid is very high, the conversion of palmitic acid, X_A, attains to the equilibrium within 20 min. The initial rate of pellets is a little lower than that of particles due to the decrease of ion-exchange capacity. However, the conversion for pellets exceeds that for particles at the reaction time over one hour because the equilibrium constant of water adsorption, K_W, is very low.

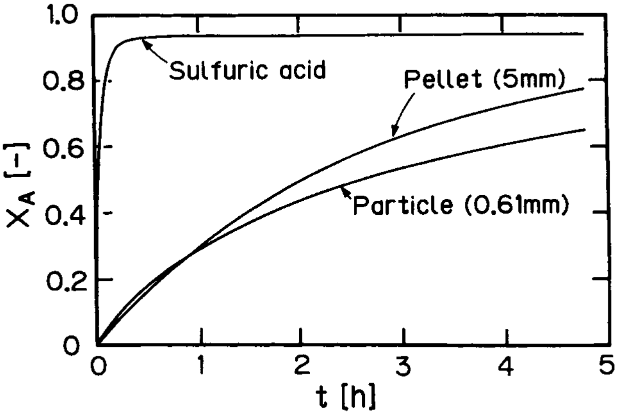

Figure 6. Comparisons of catalytic activities among resin particles, pellets, and sulfuric acid. (T = 380 K, C_{AO} = 1250 mol/m^3, C_c = 65.8 mol/m^3, M = 5, and W_O = 0).

Conclusion

Ion-exchange resin pellets with 5 mm diameter were made by mixing ion-exchange resin particles with binding powders. Catalytic activity of resin pellets was compared with that of resin particles and sulfuric acid for the esterification of palmitic acid with isobutyl alcohol in a batch reactor. Although the activity of pellets is lower than that of sulfuric acid, it is easy to separate the catalyst from reaction mixtures. Since polyethylene as a binder has a hydrophobic property, resin pellets are superior to resin particles at higher conversions. Therefore, resin pellets are useful to operate fixed-bed reactors with lower pressure drops.

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